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Surface forces arising from adsorbed hydrolysis products of metal ions in ZrO_2 and silica dispersions: Cu(II), Ni(II), Co(II) and Al(III)

YeeKwong Leong

Chemical and Processing Engineering School of Mechanical Engineering, University of Western Australia, Crawley, Australia, 6009

Abstract

The effects of hydrolyzable Cu^{2+}, Co^{2+}, $Ni^{2+}$and Al^{3+} ions on the zeta potential and yield stress behaviour of ZrO_2 and SiO_2 dispersions were evaluated as a function of pH. With ZrO_2 dispersion, adsorbed hydrolysis product of Cu^{2+} increases the yield stress at zero zeta potential while that of Al(III) decreases it. As the particles are completely coated with hydrolysis product, the most probable explanation for the stronger attraction between ZrO_2 particles coated with Cu^{2+} hydrolysis products must be due to an increase the effective Hamaker constant of particle in water. In the case of ZrO_2 particles coated with Al^{3+} hydrolysis products, the effective Hamaker constant is decreased. Silica dispersions are not flocculated even at its point of zero charge of pH ~2.0. However this dispersion is flocculated by the adsorbed hydrolysis products of Co^{2+} and Ni^{2+} ions. The onset of flocculation corresponded to the pH of formation of the hydrolysis products. With silica dispersions, at low coverage of hydrolysis product, the attractive forces contributing to the yield stress are charged patch and bridging. At high surface coverage at the pH of maximum yield stress, the increased in the effective Hamaker constant by the hydrolysis product is responsible for the enhanced van der Waals attraction.

Keywords: Yield stress; Zeta potential; Hydrolysis products of metal ions; Adsorption; Surface forces

1. Introduction

Metal ions hydrolysis products have a range of industrial applications and can be used to alleviate environmental concerns of heavy metal pollution. Hydrolysis products of Al(III) and Fe (III) ions are often used as coagulant and flocculant in wastewater treatment. Coating of TiO_2 paint pigment with silica and alumina is normally produced by calcination of the TiO_2 particles containing the adsorbed metal ions hydrolysis products. The surface area of a catalyst oxide material can be greatly increase by impregnating a porous substrate support with a solution of the metal ions and then hydrolysed the metal ions, followed by calcination. The strong affinity of the metal ions hydrolysis products to adsorb is a common mean of removing heavy metal ions from wastewater.

James and Healy [1,2] measured the adsorption behaviour of a range of cations, Ca^{2+}, Co^{2+}, Fe^{3+}, La^{3+} and Th^{4+}, on silica in dispersion. The effects of these adsorbed ions on the electrokinetic properties of silica dispersion were also determined. For each metal ion there was a critical pH where adsorption increased from 0 to 100% occurring over very narrow pH range of ~1 pH unit. This critical pH is usually just below the pH of the formation of the first hydrolysis product [1]. Adsorption of Co(II) gave rise to three points of charge reversal (CR1, CR2 and CR3) [2]. CR1 is the isoelectric point of the silica substrate. CR3, the positive to negative charge reversal, is the point-of-zero charge of the metal hydroxide at complete surface coverage. CR2, the negative to positive charge reversal occurred at pH just before the pH of bulk hydroxide precipitation. James and Healy [2] proposed a model of surface-induced metal hydroxide precipitation to account for the metal ions adsorption at pH below bulk precipitation of hydrolysis product.

Adsorption of the hydrolyzable metal ions was also found to affect coagulation rate [3–6] and flotation recovery [7]. Like adsorption, there is a narrow pH range where flotation recovery passes from zero to 100% [8,9]. Clearly the nature and strength of the interparticle forces between particles containing adsorbed hydrolysis products will have an important effect on coagulation and flotation behaviour. However no work on interparticle force arising from hydrolysable cations characterization has been done so far. This paper aims to address this issue.

The effects of anions and cations on the yield stress or interparticle forces of concentrated oxide dispersions were only recently investigated. Franks et al. [10] studied the effects of IO_3^-, BrO_3^-, Cl, NO_3^-, and ClO_4^- on yield stress of a-Al_2O_3

E-mail address: yee-kwong.leong@uwa.edu.au.

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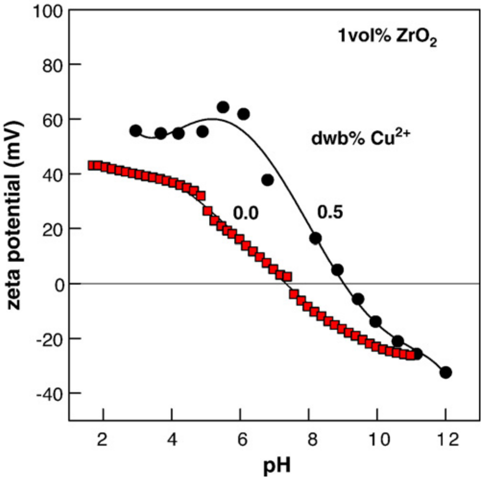

Fig. 1. The zeta potential versus pH behavior of ZrO_2 dispersion in the presence of 0.5 dwb% Cu(II) ions.

suspensions at high ions concentration. Structure maker ions (IO_3^- and BrO_3^-) produce a stronger particle network compared with structure breaker ions (Cl^-, NO_3^-, and ClO_4^-). The van der Waals attractive force is unable to account for the high yield stress displayed in the presence of IO_3^-. An additional attractive force was suggested.

Franks [11] also reported the yield stress and zeta potential behaviour of silica dispersions under the influence of concentrated Li^+, Na^+, K^+, and Cs^+ions with Cl^-as the co-ion. Adsorption of the poorly hydrated ions, K^+, and Cs^+, is larger and bring about charge reversal at high electrolyte concentrations. The yield stress at high pH was found to increase in the order $Li^+<Na^+<K^+<Cs^+$. The least hydrated ions produced the largest yield stress. Van der Waals attraction cannot account for this high yield stress value. An ion–ion correlation force was attributed as the additional attractive force.

Mpofu et al. [12] investigated the effect of hydrolyzable Mn(II) and Ca(II) ions adsorption on the surface chemistry, particle interactions, flocculation, and dewatering behavior of kaolinite dispersions at pH 7.5 and 10.5. Metal ion adsorption significantly influenced adsorption, yield stress, settling rate, and consolidation of kaolinite slurries. The presence of Mn(II) and Ca(II) ions alone led to a systematic reduction in zeta potential as a result of specific adsorption of positively charged metal hydrolysis products at the kaolinite–water interface. This led to a lower dispersion yield stress and improved clarification but was found to have no effect on sediment consolidation.

In this study, the effects of hydrolysable Cu(II), Ni(II), Co(II) and Al(III) ions on the yield stress of oxide dispersions were evaluated. A range of hydrolysis products are formed by these cations. For each metal ions, the nature of the hydrolysis products is very pH-dependent [13].

2. Materials and method

Oxides used were ZTech ZrO_2 and Sigma fumed silica. The ZrO_2 and silica have a median particle size of 250 and 50 nm, and a BET surface area of 15.4 and 200 m^2/g respectively. AR grade soluble salts of Cu(II), Co(II), Ni(II) and Al(III) were used. In the dispersion preparation a solution of accurately known concentration of metal ions was first prepared by dissolving a known amount of the metal salt in acidified Milli-Q water of accurately known mass. The solution was kept at pH 2.0 with the addition of a few drops of concentrated nitric acid to prevent the formation of hydrolysis products. Then a known mass of the fumed silica powder was added to the solution. The dispersion was sonicated for about 1 min using an ultrasonic processor with a 1/2 inch horn. The prepared dispersion was allowed to stand for about 2 hours before the yield stress measurement. The dispersion pH was increased step-wise with 1 M to 10 M KOH solutions. The added KOH droplets were dispersed by sonication. At each pH interval, the yield stress of the dispersion was measured with the vane rheometer [14]. For zeta potential measurements with a Matec Acoustosier, ZrO_2 dispersions containing 1.0 vol.% solids were used.

3. Results and discussion

3.1. Cu(II) ions

The effect Cu(II) on the zeta potential of ZrO_2 dispersion is shown in Fig. 1. The oxide has an isoelectric point at pH 7.0. The addition of 0.5 dwb% Cu(II) shifts the pH of zero zeta potential from 7.0 to 9.0. Adsorption of a positively charged species usually causes such a shift [15].

The corresponding yield stress versus pH plot is shown in Fig. 2. Included in the plot is the result for ZrO_2 dispersion without added metal ions. This dispersion displayed a maximum yield stress of 450 Pa at pH of 7.0. At this pH only the van der Waals attractive force is present. The dispersion with 0.5 wt.% Cu(II) displayed a much larger maximum yield stress of ~ 750 Pa at pH 9.1. In both cases the maximum yield stress is located at the pH of zero zeta potential. The attractive force between the particles with the adsorbed Cu(II) hydrolysis product is therefore much stronger.

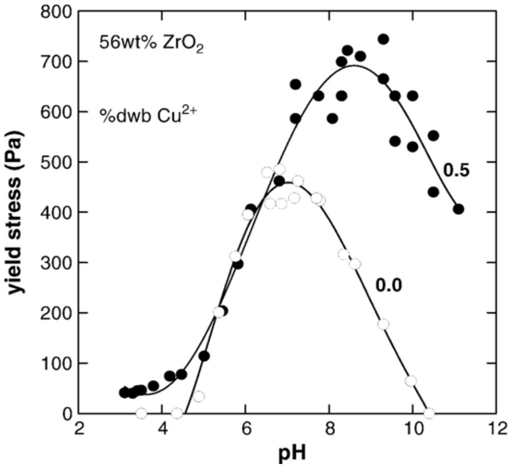

Fig. 2. The yield stress versus pH behaviour of ZrO_2 dispersion with and without Cu(II) added.